Chapter 10

Electrostatic Assembly of Polyelectrolytes on Electrospun Fibers

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Electrostatic layering of polyelectrolytes and charged titanium dioxide nanoparticles was demonstrated on the surface of polyacrylonitrile nanofibers. The surface chemistry of the electrospun fibers was modified by immersing them in a heated aqueous solution of 1.0 N sodium hydroxide. The resulting surface groups of carboxylic acid were then used to build alternating layers of polycations and polyanions to form nanometer-scale composite archetechtures. Since the polyacrylonitrile in the nanofibers were not entirely converted to acrylic acid, the fibers remained insoluble in water, unlike electrospun polyelectrolytes. This difference allows layer-by-layer assembly that pure polyelectrolyte nanofibers do not.

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Introduction

Recognizing that electrospinning alone cannot produce nanometer-scale structures for a number of applications, this work has sought to expand the utility of electrospinning by combining it with the electrostatic layer-by-layer assembly technique. Polyelectrolytes and other electrostatically charged entities can be permantly adsorbed onto the surface of an electrospun fiber and complex nanoscale layers on a nanofiberous membrane can result.

Electrospinning

Electrospinning uses a high voltage applied to a viscous polymer solution to create electrically charged jets . These jets dry to form very fine polymer fibers, which are collected on a target as a non-woven membrane. The diameters of electrospun fibers can range anywhere from several micrometers to as narrow as tens of nanometers depending on the polymer and experimental conditions. As a result, electrospun nanofibrous membranes can have a surface area per unit volume of up to two orders of magnitude higher than that of continuous thin films.

Many polyelectrolytes are difficult to electrospin as they require significant amounts of water to solvate them. Because of its high surface tension, water can be problematic as a spin-dope solvent, causig the jet to collapse. A high surface tension solvent tends to cause the spinning jet to collapse, or partially collapse into droplets. This can be ameliorated somewhat by mixing water with a lower surface-tension solvent such as ethanol or N,N dimethyl-formamide (DMF). Polyacrylic acid and sulfonated polystyrene have been successfully electrospun using mixed solvents of water and organics.

Electrospun nanofibers of polyelectrolytes are, however, unsuitable for subsequent layer-by-layer LBL assembly because they dissolve when immersed in the appropriate counter-ion solution. Because of this observation, an alternative approach of functionalizing the nanofiber surface was used in this research. While this added a processing step, it has the advantage of creating an insoluble nanofiberous membrane with electrolyte groups on the surface suitable for electrostatic assembly.

Electrostatic layer-by-layer Assembly

Layers of polyelectrolytes may be deposited onto an electrostatically charged substrate by alternately dipping it in polycationic and polyanionic

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solutions. As the substrate is immersed in each solution, the polyions complex together to form an insoluble polymeric salt on the substrate. A diagram illustrating the layer-by-layer technique is illustrated in Figure 1. The illustration shows an anionic substrate, a cationic substrate is equally feasible, but would be dipped in the solution in the opposite sequence. Because not all of the ionic groups in any one layer are complexed with the underlying layer, the new surface retains the charge of the last electrolyte applied. Electrostaticly assembled structures are often described in terms of numbers of bilayers, where a bilayer is a cationic layer paired with an anionic layer. This method was first reported by Decher *et al.*[i,ii] and has garnered much interest and research attention in the last decade, including several review articles.[iii]
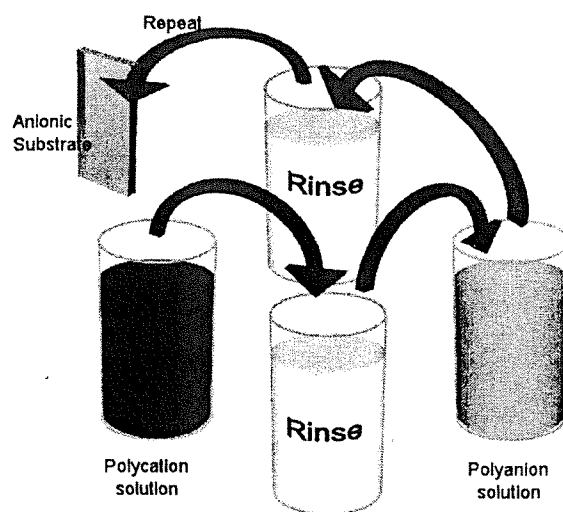

Figure 1. Diagram of electrostatic layer-by-layer assembly dipping sequence, shown for an anionic substrate.

Dubas and Schlenoff presented a study of the factors affecting the multilayer growth process[iv]. They used the strong polyelectrolytes polystyrenesulfonate (sodium salt) and poly(diallyl-dimethylammonium chloride). Low molecular weight salts were used to shield some of the charged groups on the polyelectrolytes. Film thickness was found to scale proportionately with the number of bilayers deposited and with salt concentration, *i.e.* increased salt concentration caused the individual layers to be thicker. The shielded ionic groups on the polymers do not complex with each other, resulting in longer segments of the polyelectrolyte chain free to adopt conformations with larger interaction volumes. They also indicated that localized rearrangements of the adsorbed polymer were possible due to the low molecular weight salt adsorbing

and desorbing onto the substrate at the ionic sites. However, they used labeled polyelectrolytes to show that the polymers, once adsorbed do not desorb and exchange with polymers in solution.

This was different from the approach taken by Michael Rubner and coworkers in using weak polyelectrolytes and controlling the pH of the solution, rather than strong electrolytes and salts to impart the desired properties in the final film.[v,vi]

Techniques

Electrospinning

A spin-dope of 8 weight percent polyacrylonitrile in DMF was prepared and electrospun at 20 to 25 kV. The spin dope was held in a horizontal glass pipette with the high-voltage electrode inserted in the top. Electrospinning targets used were copper mesh or tin-oxide coated glass slides. In samples for TEM imaging, electrospun membranes were prepared directly on copper TEM sample grids. Figure 2 illustrates the electrospinning apparatus used for this work.
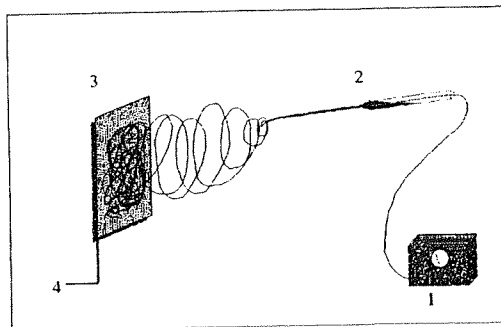

Figure 2. Electrospinning set-up (1: power source; 2:pipette and polymer spin-dope solutions; 3: collection target; 4: ground)

Surface Functionalization

The electrospun membranes of PAN nanofibers were immersed in a 1.0N sodium hydroxide (NaOH) solution at 80°C for 20 minutes to functionalize the surface with carboxylic acid groups. Upon removal, the membranes were rinsed with de-ionized water until the rinse water had a pH of 7 as measured by an electronic pH meter.

The surface functionalization reaction used was the well known conversion of cyano groups into carboxylic acid by exposure to strong alkali. The reaction scheme of cyano groups with hydroxy anions to form carboxylic acid groups is outlined in Figure 3. Electrospun membranes immersed in the NaOH solution turned brown after a few minutes. This color change has been reported as indicative of the presence of heterocyclic intermediates in the formation of carboxylic acid groups.[vii]
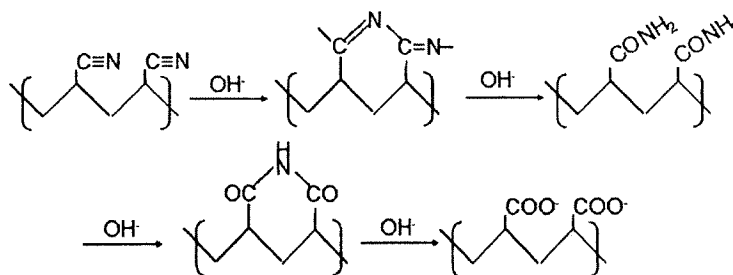

Figure 3. Reaction scheme for surface functionalization of polyacrylonitrile to polyacrylic acid (from ref. vii).

Electrospun membranes did not exhibit any morphological changes following treatment with sodium hydroxide. SEM images of electrospun membranes of PAN prior to functionalization and after being surface functionalized are shown in Figure 4. Following the surface treatment reaction, the nanofibers were completely insoluble in a number of solvents, including water, DMF, ethanol, and chloroform. Untreated PAN nanofibers dissolved immediately when immersed in DMF. This insolbility suggests the presence of cross-linked intermediate functionality present in the fiber. It is believed the nanofibers consist of a core of unmodified poyacrylonitrile and a surface of ionic carboxylic acid (or sodium salt analogue) groups with the intermediate reaction products in the intermediate layers.

SEM-UML   1μm   10KeV   X10000   SEM-UML   1μm   10KeV   X10000
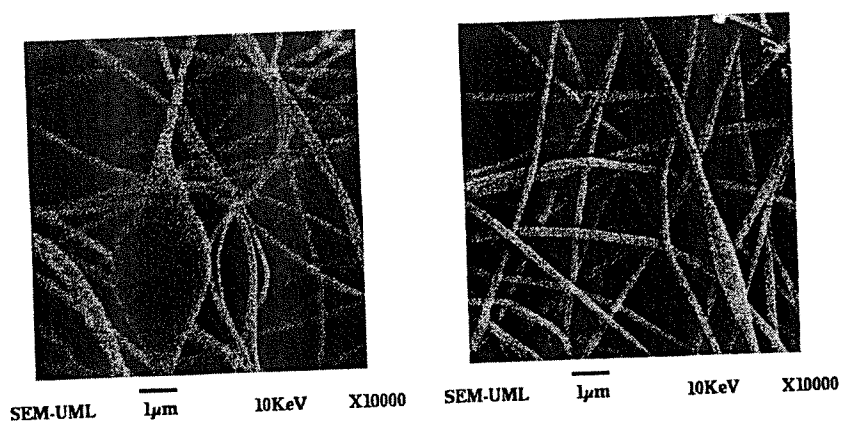
Figure 4. SEM images of polyacrylonitrile fibers, as spun (left) and of carboxylic acid-functionalized polyacrylonitrile fibers (right).

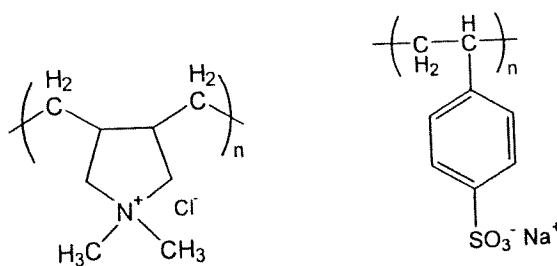Figure 5. Chemical structure of poly(diallyldimethylammonium chloride)(PDAC)(left) and sulfonated polystyrene (SPS)(right) .

Electrostatic Assembly

Charged particles of titanium dioxide, carboxylic acid functionalized hematin, and the polyelectrolytes: sulfonated polystyrene (SPS) (molecular weight 1,000,000 g/mol) and poly(diallyldimethylammonium chloride)(PDAC) (molecular weight 500,000-750,000 g/mol) were assembled on the nanofiber surface by LBL deposition. The chemical structures for PDAC and SPS are shown in Figure 5. Titanium dioxide nanoparticles were ground with a mortar and pestle together with 5N HCl (1g TiO_2 to 20ml). This solution was diluted 40 times with deionized water. The functionalized membranes were immersed in the diluted TiO_2 suspension for one minute and then rinsed with deionized water. Membranes were immersed in solutions of SPS and PDAC with concentrations of 0.1 weight percent for 10 minutes and then rinsed in de-ionized water. Carboxylic acid-functionalized hematin was prepared in a buffer solution at pH 11 and was used as an anion in place of SPS.More evidence of successful surface functionalization of PAN nanofibers was the application of electrostatic layer-by-layer assembly. This would not have been possible without ionic, or ionizable, surface groups on the nanofiber surface. Following electrostatic assembly, the surface area of the nanofibrous membrane was largely retained. Electron microscope images of 1 PDAC/SPS bilayer applied to the fiber surface can be seen in Figure 6. Figure 7 and Figure 8 show functionalized nanofibers with 5 and 10 PDAC/SPS bilayers, respectively. It was observed that the fiber surface became rougher as more bilayers were applied. The porosity and large surface-area of the original electrospun membrane remained even after 10 bilayers were applied.
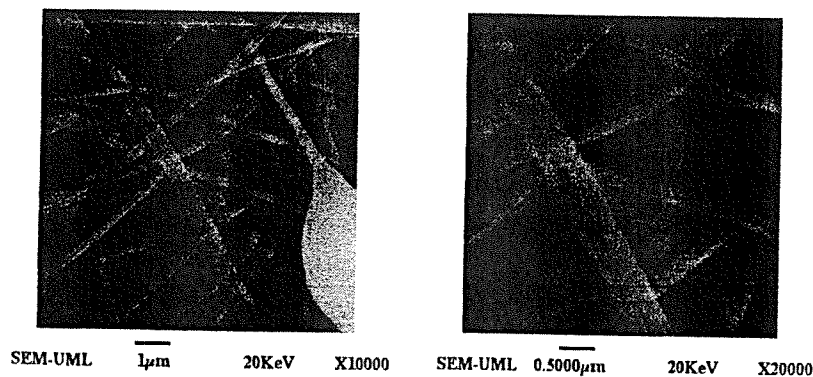
SEM-UML　　1μm　　20KeV　　X10000　　　SEM-UML　0.5000μm　　20KeV　　X20000

Figure 6. SEM images of carboxylic acid functionalized PAN nanofibers with one PDAC/SPS bilayer applied to the surface.
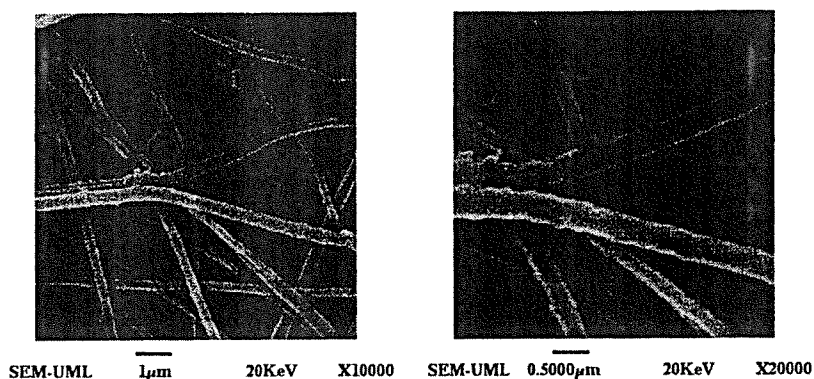
SEM-UML   1μm   20KeV   X10000   SEM-UML   0.5000μm   20KeV   X20000

*Figure 7. SEM images of carboxylic acid functionalized PAN nanofibers with
five PDAC/SPS bilayers applied to the surface.*

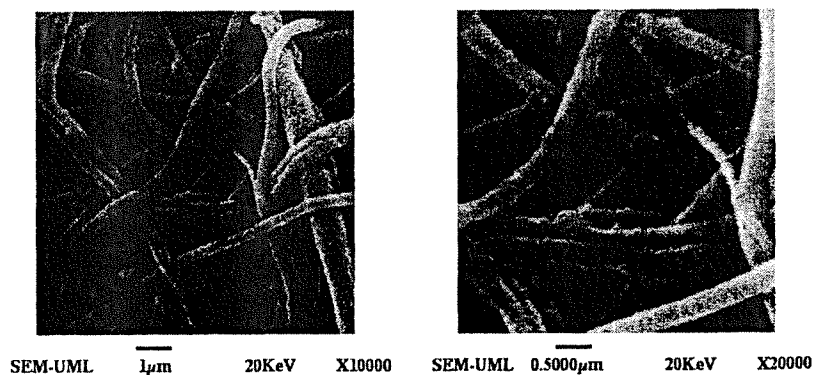SEM-UML   1μm   20KeV   X10000   SEM-UML   0.5000μm   20KeV   X20000

*Figure 8. SEM images of carboxylic acid functionalized PAN nanofibers with
ten PDAC/SPS bilayers applied to the surface.*

In addition to polyelectrolytes, it was possible to electrostatically assemble
charged titanium dioxide particles onto the functionalized PAN surface.
Cationic TiO_2 particles were found to sparsely adsorb to the surface of the
anionic-functionalized PAN nanofibers. The particles were rendered cationic by
grinding commercial TiO_2 particles in strong hydrochloric acid and then diluting
the paste to a liquid. The pH of the liquid remained low and was likely
responsible for the sparse coverage of the fibers by the TiO_2 particles. To
overcome this, a new membrane was prepared and five bilayers of PDAC/SPS
were assembled on the nanofiber surface prior to immersion in the titanium

dioxide suspension. Since SPS remains anionic over a much wider pH range, more anionic sites should have been available to complex with the positively charged TiO$_2$ particles. This behavior was observed and is shown in SEM images in Figure 9 and in TEM images in Figure 10 showing reasonably complete particle coverage. Coverage remained incomplete in the five bilayer samples. Energy dispersive X-ray spectroscopy (EDS) of the same sample confirmed the presence of sulfur from the SPS where gaps in the TiO$_2$ particle coverage were observed.
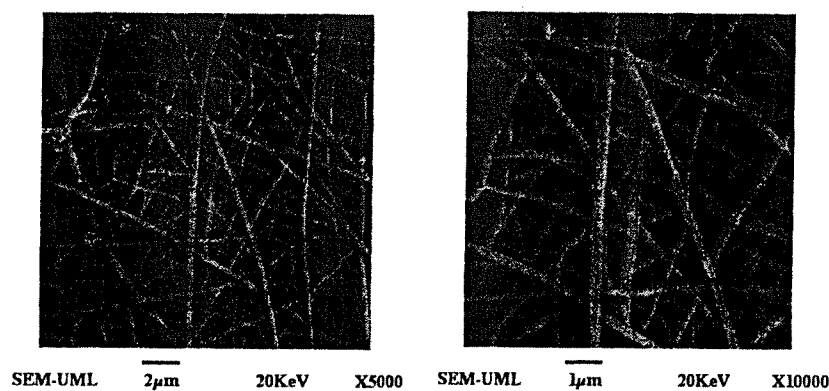

| SEM-UML | 2μm | 20KeV | X5000 | SEM-UML | 1μm | 20KeV | X10000 |

Figure 9. SEM images of cationic TiO$_2$ assembled onto 5 bilayers of PDAC/SPS on top of functionalized PAN nanofibers.
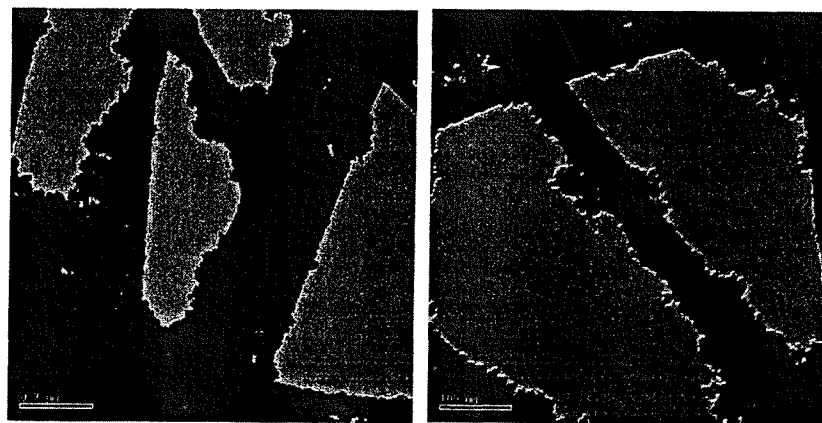

Figure 10. TEM images of cationic TiO$_2$ assembled onto 5 bilayers of PDAC/SPS on top of functionalized PAN nanofibers.

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Hematin was used in LBL deposition and can be employed as a catalyst in conjugated polymer synthesis. Hematin functionalized with carboxylic acid groups can be electrostatically layered as an anion at pH 11. At this pH it is colored a brownish green and has an absorbance peak around 395 nm. As such, it was used to spectroscopically monitor successful electrostatic layer-by-layer assembly on a functionalized PAN electrospun membrane. To accomplish this, a glass slide was coated in a thin electrospun membrane of carboxylic acid-functionalized PAN and then placed in a cuvette in the UV-vis spectrometer (Perkin Elmer Spectometer Lambda 9) with a blank glass slide reference. Electrostatic assembly of the PDAC and hematin layers was done in the cuvette to minimize errors associated with changing the angle between the incident beam and the glass slide.

The absorbance spectrum is shown in Figure 11. With each additional hematin layer the 395 nm peak absorbance increased. Assembly of the PDAC cationic layer caused a slight decrease in absorbance in the same region. This was attributed to scattering of the incident beam by the PDAC layer decreasing photon access to the underlying hematin layer to a small degree. PDAC should not show any absorbance in this wavelength range. The non-zero absorbance of the first layer of PDAC on the electrospun fibers was likely due to scattering of the incident beam by the fibers themselves, since the membrane almost certainly contained fibers with diameters in the 100 to 500 nm range.

The increasing absorbance at 395 nm exhibited good linearity with sequential addition of hematin layers as shown in Figure 12. This indicated that approximately the same amount of hematin was deposited with each assembled layer. Thus, it can be inferred that the ionic character of the fiber surface was renewed with each addition of PDAC and hematin, indicating successful LBL assembly.

Conclusions

Electrostatic LBL assembly has been demonstrated on electrospun nanofiber surfaces. A variety of polymer electrolytes, charged metal oxide particles, and the biocatalyst hematin were successfully adsorbed. It is believed any ionic material reported in the literature used in electrostatic LBL assembly of films can also be applied to electrospun fibers. The key to this success was the surface-functionalization of the nanofiber with carboxylic acid groups. This simple, one-step reaction in sodium hydroxide created an insoluble nanofibrous membrane with a surface suitable for electrostatic assembly and a core rugged enough to survive the assembly process. It is postulated that similar results could be obtained by adding a crosslinking agent to a suitable polyelectrolyte spin-dope and crosslinking the nanofibers after electrospinning. However, this may involve more complicated spin-dope solutions and electrospinning processes. Thus, it may be possible to obtain nanofibers with alternate surface chemistries and gel-like fibers.
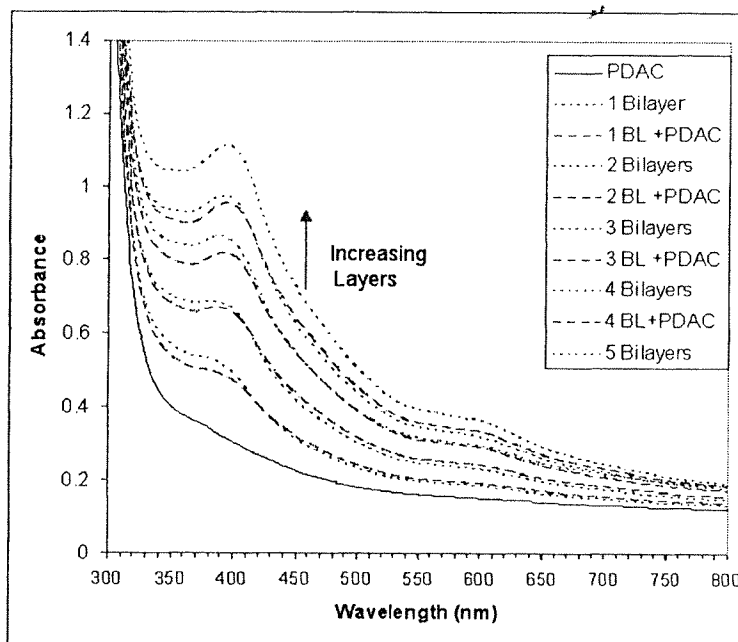
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Figure 11. UV vis spectrum of electrospun functionalized PAN with PDAC and hematin adsorbed on the fiber surface.
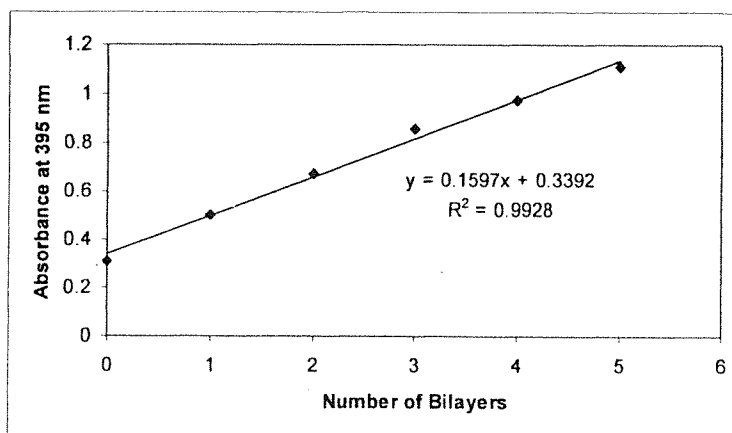

$y = 0.1597x + 0.3392$
$R^2 = 0.9928$

Figure 12. Absorbance at 395 nm as a function of the number of PDAC/hematin bilayers on an electrospun membrane.

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Acknowledgements

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